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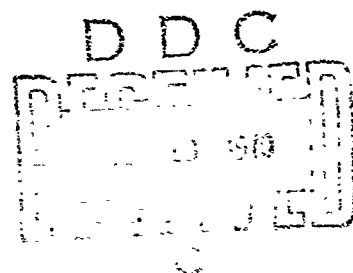
**PHASE EQUILIBRIA INVESTIGATION OF
BINARY, TERNARY, AND HIGHER
ORDER SYSTEMS**

**PART VIII. THE STRUCTURE OF A TERNARY PHASE T_3C_2
IN THE V-Ta-C SYSTEM**

E. RUDY

TECHNICAL REPORT AFML-TR-69-117, PART VIII

APRIL 1970



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IN THE V-T α -C SYSTEM**

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FOREWORD

The experimental research described in this technical report was carried out at the Materials Research Laboratory, Aerojet-General Corporation, Sacramento, California, under USAF Contract AF 33(615)-67-C-1513. The contract was administered under the direction of the Air Force Materials Laboratory, with Capt. P.J. Marchiando (MAMC) as Project Engineer, and Dr. E. Rudy, Aerojet-General Corporation (now at the Oregon Graduate Center, Portland, Oregon) serving as Principal Investigator.

The author wishes to acknowledge the help of Messrs J. Pomodoro (fabrication of samples), R. Cristoni (preparation of drawings), and of Mrs. J. Weidner, who typed the report.

The manuscript of this report was released by the author December 1969 for publication.

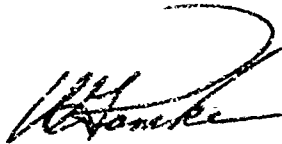
Other reports issued, or in preparation, under USAF Contract AF 33 (615)-67-C-1513, include:

- | | |
|-----------|--|
| Part I. | The Phase Diagrams of the Systems Ti-Nb-C, Ti-Ta-C, and Ti-Mo-C. |
| Part II. | Effect of Re and Al Additions on the Metal-Rich Phase Equilibria in the Ti-Mo-C and Ti-Nb-C Systems. |
| Part III. | Phase Studies in the V-Ta-C and Nb-Ta-C Systems. |
| Part IV. | Effect of Mo and W Additions on the Subcarbide Solid Solutions in the V-Ta-C and Nb-Ta-C Systems. |
| Part V. | The Phase Diagram of the W-B-C System. |
| Part VI. | The Phase Equilibria in the Metal-Rich Region of the Hafnium-Tantalum-Nitrogen System. |

FOREWORD (Continued)

Part VII. The Phase Diagram Ti-V-C.

This technical report has been reviewed and is approved.



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ABSTRACT

The crystal structure of Ta_2VC_2 was determined from X-ray powder photographs. The structure is trigonal, space group D_{3d}^5 - $R\bar{3}m$, with a rhombohedral unit cell of $a_R = 7.481 \text{ \AA}$, $\alpha = 23^\circ 27'$ (hexagonal axes $a = 3.045 \text{ \AA}$, $c = 21.81 \text{ \AA}$). The unit cell contains 9 close packed metal layers in stacking sequence $(hkc)_3$, or ABABCBCAC. The metal atoms are statistically distributed among point positions 3(a) and 6(c). It was not possible to decide by X-ray diffraction whether the carbon atoms are randomly distributed among the 9 octahedral interstitial sites in 6(c) and 3(b), or whether an ordered sublattice structure is formed.

The phase is stable from room temperature to above 2600°C . The homogeneity range of 1650°C varies between the limits $(\text{Ta}_{1.89} \text{ to } 2.04, \text{V}_{1.20} \text{ to } 0.96)\text{C}_{1.74} \text{ to } 1.80$; the phase is thus substantially deficient in carbon.

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I. INTRODUCTION

Examination of X-ray powder photographs of specimens used in DTA studies of the sublattice order-disorder transformations in tantalum-rich $(V, Ta)_2C$ solid solution alloys revealed the occasional occurrence of reflections not identifiable with the patterns of the known phases in the system. The samples showing these extra reflections were chemically analyzed and found to contain more than 33 At.% carbon; thus indicating as location for the unknown phase the composition region between the subcarbide and the monocarbide solid solution. Additional alloys did indeed confirm the existence of a new ternary carbide at the approximate composition $Ta_{0.22}V_{0.41}C_{0.37}$.

Attempts to grow single crystals from the melt for X-ray diffraction studies were unsuccessful because, as a more detailed investigation revealed, the phase is not stable at solidus temperatures. A clarification of the crystal structure was therefore attempted from powder photographs.

II. EXPERIMENTAL

Approximately 30 experimental alloys, containing between 34 and 40 At.% carbon, 10 and 30 At.% vanadium, and the balance tantalum, were prepared by short duration hot pressing of the powder mixtures in graphite dies. The alloying ingredients were elemental tantalum and the monocarbides of vanadium and tantalum.

Vanadium monocarbide was obtained by reacting compacted mixtures of vanadium metal and graphite powder at temperatures between 1600°C and 1750°C in a graphite element furnace under a vacuum of 5×10^{-6} Torr. The vanadium metal powder used in the preparation of the carbide was purchased from Oregon Metallurgical Corporation, Albany, Oregon. The overall purity

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was better than 99.6%. Major contaminants were oxygen (1780 ppm), carbon (350 ppm), and nitrogen (320 ppm). The contaminant level in the spectrographic grade graphite powder (Union Carbide Corporation, Carbon Products Division) was below 2 ppm. The as-prepared vanadium monocarbide had a total carbon content of 48.6 At.%, of which 1.6 At.% were present as elemental graphite. The lattice parameter of the product was $a = 4.172 \text{ \AA}$.

Tantalum monocarbide, purchased as 10 μ powder from Wah Chang Corporation, Albany, Oregon, was acid-leached to remove soluble constituents and high-vacuum degassed (2 hrs at 4×10^{-6} Torr at 2200°C) to eliminate volatile contaminants. The lattice parameter of the purified product was $a = 4.4560 \pm 0.003 \text{ \AA}$. The carbide contained 6.15 wt.% carbon, with 0.04 wt.% present as free graphite. The following impurities (in ppm) were found in the processed material: Ti-400; Nb-150; Y-200; O-<20; N-<10; H-not detected; Cr-<25; Co-40; Fe-<70; sum of B, Mg, Mn, Ni, Pb, Si, and Sn-<50.

The surface-cleaned specimens were heat treated at 1350°C, 1500°C, 1650°C, and 2000°C. The times at temperature varied between 5 and 90 hours. For studies of the high temperature stability of the new carbide phase, selected specimens were exposed for short times to temperatures as high as 3000°C.

X-ray powder photographs using Cr-K α and Cu-K α radiation were prepared from all experimental alloys and about half of the specimens were chemically analyzed.

III. RESULTS

A. PHASES AND PHASE STABILITIES

In the alloy series heat treated at 1650°C, the specimens containing 37 At.% carbon and between 20 and 25 At.% vanadium were homogeneous and the X-ray photographs revealed only the pattern of the new ternary carbide

($T_3C_2^*$, T = transition metal). The observed angular shift of the diffraction maxima with the metal exchange also points to the existence of a noticeable homogeneity range at the selected equilibration temperature. A sample with slightly higher vanadium content, Ta-V-C (35-27-38 At.%), consisted predominantly of monocarbide, besides smaller quantities of T_3C_2 and subcarbide, whereas another alloy Ta-V-C (32-31-37 At.%) contained only a mixture of TC and T_2C . The T_3C_2 phase thus appears to be restricted by a three-phase equilibrium $T_3C_2 + TC + T_2C$ towards vanadium-rich compositions.

Phases observed in specimens located near the tantalum-carbon edge binary included T_3C_2 , $\zeta^{(1)}$, TC, and T_2C . The T_3C_2 -phase is separated by an extended two-phase field from the subcarbide solid solution, and also forms two-phase equilibria with the monocarbide and the ternary ζ -phase.

The principle phase relationships derived from an alloy series equilibrated at 1900°C were the same as at 1650°C. At 2000°C, however, the ternary ζ -phase was not detected in any of the specimens, and the only phases found to partake in the equilibria were T_3C_2 , T_2C , and TC.

The T_3C_2 phase was consistently observed in alloys exposed to temperatures up to 2600°C, but not in alloys which were equilibrated for a short time (~2 min) at 2800°C and 3000°C and then rapidly cooled. These findings indicate a termination of the phase in a solid state reaction between 2600°C and 2800°C, since melting at this composition occurs approximately 300°C higher.

B. DETERMINATION OF THE CRYSTAL STRUCTURE

An inspection of the X-ray powder photographs of the new phase revealed a pronounced similarity with the diffraction pattern of the hexagonal

(*) Ideal composition based on structure

subcarbide. Certain reflections coincided in location and intensity with those of the subcarbide solution at the equivalent metal exchange, while others, of weaker individual intensity, appeared in clusters around seemingly relatable diffraction maxima in the T_2C phase. It also was noted that only those diffraction maxima appeared unchanged in the pattern of the new phase which were common to both the hexagonal and the cubic close packed lattice.

These observations suggest the same building principle as in the subcarbide and the monocarbide, namely closest packing of the metal atoms, with the carbon atoms filling the octahedral interstices in the metal lattice. The structural relationships suggest the a -axis of the new phase to correspond closely to the a -axis of the subcarbide at the equivalent metal exchange, or about 3.04 \AA ; and the c -axis to be, approximately, a multiple of the layer spacing in Ta_2C ($l_h \sim 2.4 \text{ \AA}$).

Indexing of the Cu-K α powder pattern of an alloy Ta-V-C (40-23-37 At. %) on the basis of a hexagonal unit cell of $a = 3.045 \text{ \AA}$, and $c = 21.81 \text{ \AA}$ (Table 1), accounted for all of the observed reflections. The unit cell thus contains nine, approximately equidistant, metal layers, as also evidenced by the observation that the only non-extinct $(00.l)$ reflections were those with $l = 9n$.

The systematic absences with $-h + k + l \neq 3n$ leads to a trigonal structure and a rhombohedral unit cell, $a_R = 7.481 \text{ \AA}$ $\alpha = 23^\circ 27'$, which is one-third the size of the hexagonal cell, can be chosen instead. The metal layer stacking sequence compatible with the observed unit cell is $(hhc)_3^{(*)}$. The structure proposal is thus based on space group $D_{3d}^5 - R\bar{3}m$, with (T = transition metal):

-
- (*) h = stacking as in hexagonal closest packing
 c = stacking as in cubic closest packing

Table I: Evaluation of a Powder Diffraction Pattern of Ta_2VC_2 .
Cu-K α Radiation.

Alloy: Ta-V-C (40-23-37 At.%), equilibrated for 90 hrs at 1650°C.

hk. l	$10^3 \sin^2 \theta_{obs}$	$10^3 \sin^2 \theta_{calc}$	$I_{estim.}$	$I_{calc.}$
00. 3	-	11.2	0	0.0
00. 6	-	44.9	0	0.0
10. 1	86.5	86.5	4	38.0
01. 2	90.6	90.3	2-	15.1
00. 9	101.5	101.0	4	51.0
10. 4	105.7	105.3	10	100.0
01. 5	116.8	116.5	10-	89.3
10. 7	146.5	146.4	2-	7.7
01. 8	165.7	165.1	4	14.4
00.12	-	179.6	0	0.0
10.10	210.8	210.0	4	10.5
01.11	236.2	236.2	1-	3.4
11. 0	256.2	255.9	5-6	35.4
11. 3	-	267.1	0	0.0
00.15	-	280.7	0	0.0
10.13	296.8	296.1	4-5	19.5
11. 6	-	300.8	0	0.0
01.14	329.8	329.8	4	16.7
02. 1	342.3	342.4	1-	4.4
20. 2	346.6	346.2	0-1	1.8
11. 9	357.2	356.9	6	41.5
02. 4	360.7	361.1	3,C	14.2
20. 5	372.6	372.3	3	13.8
02. 7	-	402.3	-	1.6
00.18	404.8	404.2	2	5.7
10.16	-	404.6	-	1.5
20. 8	421.3	421.0	1-	3.1
11.12	-	435.5	0	0.0
01.17	446.5	445.8	1-	2.8
02.10	466.0	465.9	1	3.0
20.11	492.7	492.1	0-1	1.1
10.19	-	535.6	-	2.6
11.15	536.3	536.5	1-2	0.0
00.21	-	550.1	-	0.0
02.13	552.1	552.0	2+	8.4
01.20	-	584.3	-	0.9
20.14	586.0	585.7	2+	8.3

Table I (continued)

hk. l	$10^3 \sin^2 \theta_{\text{obs}}$	$10^3 \sin^2 \theta_{\text{calc}}$	$I_{\text{estim.}}$	$I_{\text{calc.}}$
21. 1	598.7	598.3	1	4.6
12. 2	602.4	602.0	1-	2.0
21. 4	617.4	617.0	3	15.9
12. 5	627.9	628.2	3	15.9
21. 7		658.2		1.9
11.18	660.1	660.0	6	21.9
02.16		660.5		1.0
12. 8	677.3	676.9	1	4.3
10.22	689.2	689.0	2-	7.7
20.17	701.6	701.7	0-1	2.1
00.24	-	718.5	0	0.0
21.10	721.5	721.8	2-	4.8
01.23	745.6	745.2	4	8.7
12.11		748.0		2.0
30. 0	767.2	767.6	3-4	12.2
30. 3	-	778.8	0	0.0
02.19	792.2	791.5	1+	2.8
11.21		806.0		0.0
21.13	807.9	807.8	5	18.5
30. 6	-	812.5	0	0.0
20.20	840.9	840.1	6	1.2
12.14		841.5		21.0
10.25	867.8	864.9	6+	1.4
30. 9		868.6		15.9
00.27	909.0	909.4	2	6.4
21.16	915.3	916.4	1, C	3.6
01.26	928.8	928.5	1	4.0
02.22	944.3	944.9	4-5	17.1
30.12	-	947.2	0	0.0
12.17	956.8	957.5	3	10.6
11.24	-	974.4	0	0.0

Legend: Calculated $\sin^2 \theta$ values based on a hexagonal unit cell
 $a = 3.045 \text{ \AA}$; $c = 21.81 \text{ \AA}$.

Scale of visually estimated intensities: 0 to 10

Calculated intensities based on $I_{10,4} = 100$, not corrected
for absorption and thermal vibration.

C = Coincidence

6T in 6(c), with $z_T \sim 2/9$

3T in 3(a)

6C in 6(c), with $z_C \sim 7/18$

3(b)

Intensity calculations were carried out for a statistical distribution of vanadium and tantalum among point positions 6(c) and 3(a), as well as for an ordered metal lattice, in which tantalum occupies point position 6(c) and vanadium position 3(a). The ideal parameters, which are based on an equal spacing of the metal layers were used in the calculations. To distinguish between the possibilities, reflections (hkl) with $l = 3 + 6n$ and $l = 6 + 9n$ are especially useful, since the structure amplitudes for these planes are zero for the case of a statistical distribution, but are proportional to $f_V - f_{Ta}$ for the ordered metal lattice. Reflections like (113), (116), (11.12), and (11.15) should thus be fairly intense in the ordered phase. As these reflections were not detected in any of the diffraction patterns, however, and the calculated intensities based on a statistical metal distribution agreed better with the observed intensities, a nonpreferential occupation of the metal positions was concluded.

The carbon atoms fill octahedral interstices available in point-positions 6(c) and 3(b). These interstitial sites are arranged such that, at the ideal composition T_3C_2 , two carbon atoms are associated with three interstitial sites spaced at one-half the metal layer distance (Figure 1). This spatial arrangement suggests a distinct possibility for carbon ordering on position 6(c), with point position 3(b) remaining unfilled. As a result of the low scattering power of carbon, however, it was not possible to distinguish between an ordered or a disordered carbon sublattice.

IV. DISCUSSION

In terms of the metal sublattice, the structure of Ta_2VC_2 may be considered mediate between the hexagonal close packed subcarbide phase and the cubic close packed metal arrangement in the monocarbide. Complementary to the (hbc) stacking of the metal layers in Ta_2VC_2 is the metal structure of the homotectic phase Mo_3C_2 with a stacking sequence (cch) or ABCACBA⁽²⁾ (Figure 1). In contrast to the molybdenum carbide, however, whose structure clearly displays a sequential arrangement of hexagonal and cubic building blocks a separation of these constituent elements is not possible in the type exemplified by Ta_2VC_2 . The new structure element appearing in the latter phase is the association of two interstitial atoms with three adjacent interstitial sites spaced approximately the same as in $T_2C(h)$.

We recall that in the $T_2C(h)$ structure maximum occupancy of the interstitial sites, which are spaced at one-half the metal layer distance along the c -axis, is limited to $1/2$ (Figure 2). Higher interstitial concentrations (up to occupancy 1) can be accommodated in the cubic close packed lattice which allows for a somewhat larger spacing of the interstitial atoms $\frac{d_{cub}}{d_{hex\ ideal}} = \frac{3}{2}$. In the light of these observed regularities the $3/2$ occupancy of the octahedral sites in Ta_2VC_2 appears to be attributable to the cubic linkages between chain pieces consisting of three interstitial sites spaced as in T_2C . Closely related to the Ta_2VC_2 type are the recently clarified structures of the T_4X_3 ($X = C, N$) phases, represented by the ζ -carbides $[V(Nb, Ta)_4C_3]$ ⁽³⁾ and Hf_4N_3 ⁽⁴⁾. The structure of these phases is trigonal, with a metal layer stacking (bhcc)₃. As characteristic building element in the interstitial sublattice we find again chain pieces consisting of three octahedral interstices, but separated in this case by two, instead of one as in Ta_2VC_2 , cubically stacked carbon layers.

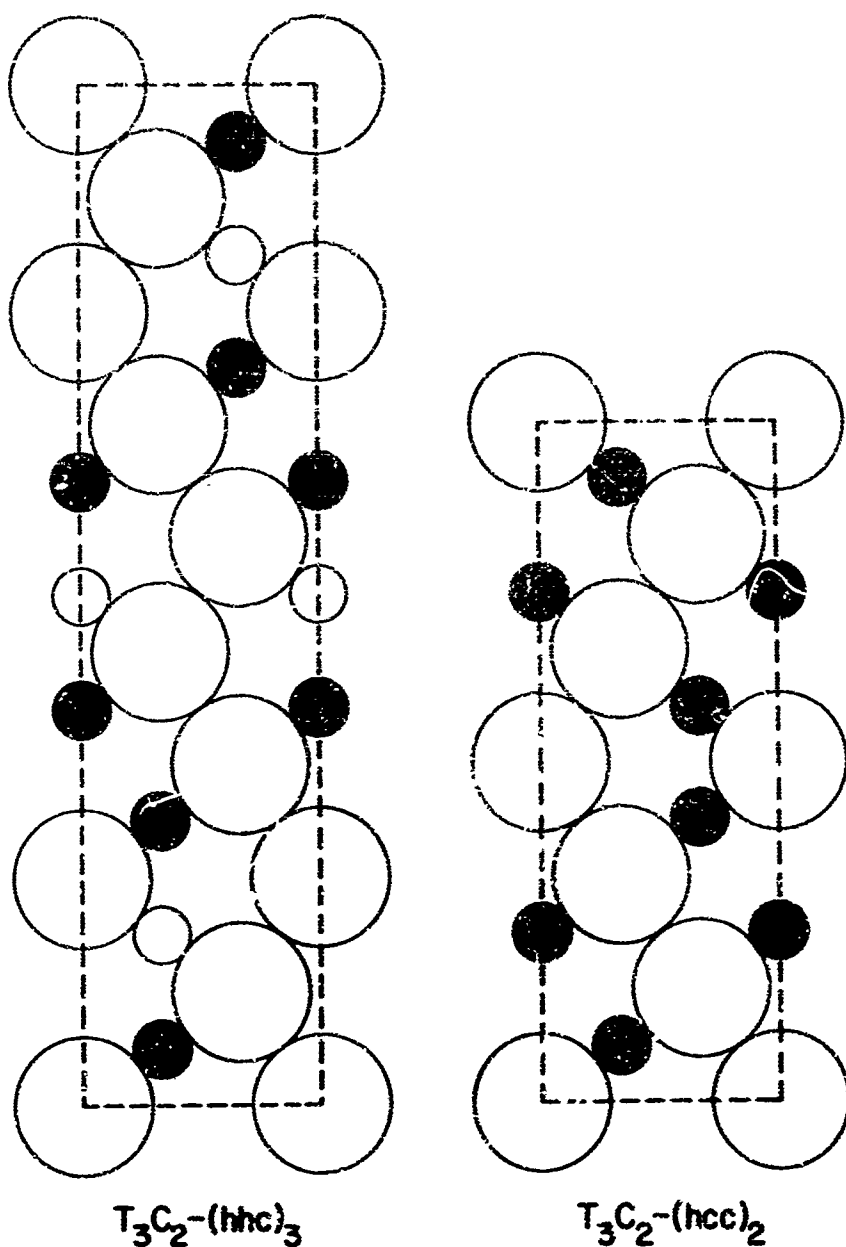


Figure 1. Sectional View of the (110) Plane of the Unit Cells of Ta_2VC_2 and Mo_3C_2 .

Left: Structure of Ta_2VC_2

Large Open Circles: Metal atoms

Small Filled Circles: Carbon atoms in 6(c)

Small Open Circles: Carbon atoms in 3(b)

Occupancy of point positions 6(c) and 3(b) is 2/3 for a disordered carbon sublattice.

Right: Structure of Mo_3C_2

Large Open Circles: Molybdenum atoms

Small Filled Circles: Carbon atoms in 2(a)

Small Shaded Circles: Carbon atoms in 4(f), 1/2 occupancy for a disordered sublattice.

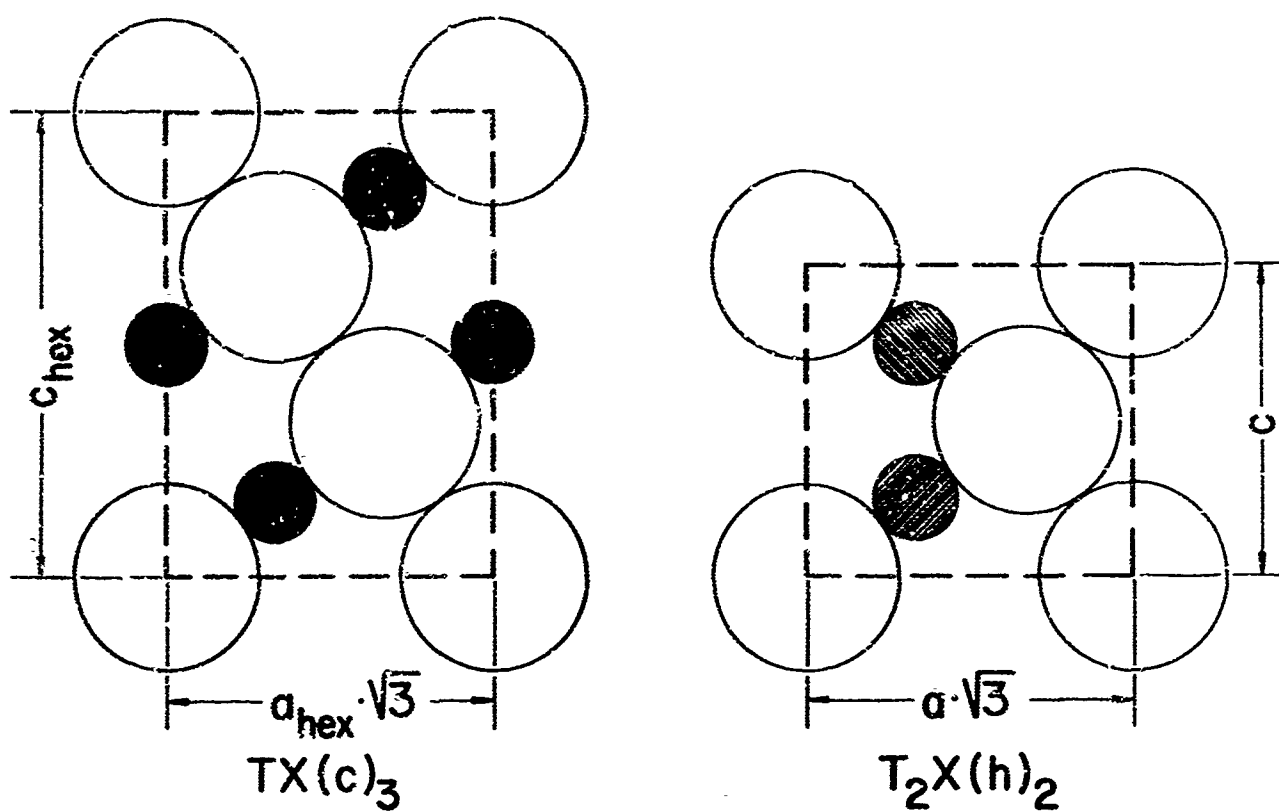


Figure 2. Cubic and Hexagonal Close Packing of the Metal Atoms in the TC and T_2C Phases (T = Transition Metal).

Large Open Circles:	Metal atoms
Small Filled Circles:	Carbon atoms
Small Shaded Circles:	Carbon atoms, 1/2 occupancy for a disordered carbon sublattice.

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